Polymer Bulletin 24, 9–16 (1990)

Polymer Bulletin

Liquid crystalline polyethers based on conformational isomerism

13. Copolyethers based on 1-(4-hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl)ethane, 1,8-dibromooctane and nonmesogenic bisphenols*

V. Percec and Y. Tsuda**

Department of Macromolecular Science, Case Western Reserve University, Cleveland, OH 44106, USA

SUMMARY

The synthesis and characterization of copolyethers based on 1-(4-hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl)ethane (MBPE), 1,8-dibromooctane and each of the following three nonmesogenic bisphenols : 3,4'-dihydroxydiphenylmethane (3,4'-BPM), 4,4'-isopropylidenediphenol (4,4'-BPA) and 3,4'-isopropylidenediphenol (3,4'-BPA) are presented. Copolymers based on MBPE, 3,4'-BPM and 1,8-dibromooctane display a nematic mesophase up to compositions containing as much as 70 mol% of 3,4'-BPM. The range of mesomorphism decreases on going from 3,4'-BPM to 3,4'-BPA and to 4,4'-BPA. These results demonstrate that structural units derived from parent amorphous and liquid crystalline homopolymers can be isomorphous within the mesophase over a certain range of copolymer composition of the resulting copolymers. Subsequently, the parameters of the mesomorphic phase transitions of these copolymers represent weight averaged values of the corresponding parameters of the parent homopolymers.

INTRODUCTION

Recently, we have advanced the concept of flexible mesogenic unit or rod-like mesogenic unit based on conformational isomerism (1-11). This concept was applied to the synthesis of liquid crystalline polyethers without flexible spacers (1), and of liquid crystalline polyethers with flexible spacers (2-11). These polymers represent the first examples of main chain liquid crystalline polymers which do not contain rigid rod-like mesogenic units (12-17). Most of these homopolyethers based on flexible spacers and flexible mesogens display only virtual mesophases (2-12). The parameters of these virtual mesophases can be determined by copolymerization experiments. Copolyethers are particularly attractive for these investigations, since their microstructure is kinetically determined (6). This is in contrast to copolyesters whose microstructure is thermodynamically controlled. So far, we provided a quantitative interpretation of the dependence of the parameters of various phase transitions on copolymer composition for copolymers based on one flexible mesogenic unit and two (2-5, 7-10), three (6) and more than three (11) flexible spacers. In all cases, when the structural units of these copolymers are isomorphic within their mesophases, the parameters of the mesomorphic phase transitions display a weight averaged dependence on copolymer composition. This concept can be used both to determine the parameters of the virtual mesophases displayed by a homopolymer (2-10) and to molecular engineer the same parameters by copolymerization (11).

Nonmesogenic units are frequently inserted within the structure of liquid crystalline copolymers to manipulate their phase transitions (12, 18-22). However, attempts to interpret the phase behavior of these copolymers in a quantitative way are not yet conclusive (19-22).

We are interested in the molecular design of novel nontraditional mesogenic units based on conformational isomerism. In order to discriminate between mesogenic units which lead the polymers displaying virtual mesophases and nonmesogenic units, we need a quantitative understanding of the phase behavior of liquid crystalline copolymers based on a mesogenic unit, a nonmesogenic unit and a flexible spacer. The goal of this paper is to discuss the synthesis and phase behavior of copolyethers based on the mesogenic unit 1-(4-hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl)ethane (MBPE), 1,8-dibromooctane and each of the following three nonmesogenic bisphenols : 3,4'-dihydroxydiphenylmethane (3,4'-BPM), 4,4'-isopropylidenediphenol (4,4'-BPA) and 3,4'-isopropylidenediphenol (3,4'-BPA).

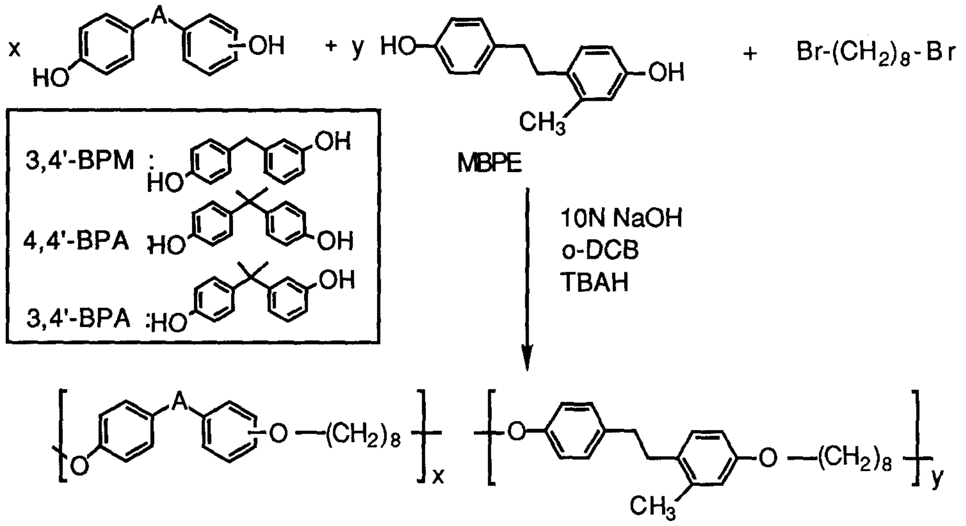
EXPERIMENTAL

The structures of the monomers and polymers are presented in Scheme I.

---

*Part 12: V. Percec and Y. Tsuda, Polymer submitted

**To whom offprint requests should be sent



Scheme I

Materials

4,4'-Isopropylidenediphenol (4,4'-BPA, 97% from Aldrich) was recrystallized from ethanol/water. 3,4'-Isopropylidenediphenol (3,4'-BPA, 100 % from Mitsui Petrochemical Industries), 3-methoxybenzoic acid (98% from Lancaster Synthesis) and 1,8-dibromooctane (98% from Aldrich) as well as the other chemicals were used as received.

3,4'-Dimethoxybenzophenone

Thionyl chloride (31.30 g, 0.263 mole) was added dropwise at room temperature to a mixture of 20.0 g (0.131 mole) of 3-methoxybenzoic acid and 300 ml of dry methylene chloride. The resulting solution was refluxed for 2 hours after which methylene chloride and the excess of thionyl chloride were removed by distillation under reduced pressure. The resulting acid chloride was dissolved in 50 ml of dry methylene chloride and added dropwise to a mixture of 21.5 g (0.199 mole) of anisole and 26.5 g (0.199 mole) of anhydrous $AlCl_3$ which was maintained below 10°C. After 3 hr of stirring at room temperature, the reaction mixture was poured into a mixture of 100 ml concentrated HCl and 400 ml ice-water. The organic layer was separated and washed sequentially with H_2O, 10% aqueous NaOH, and H_2O. After drying on $MgSO_4$, methylene chloride was removed in a rotary evaporator and the unreacted anisole was distilled under vacuum. The residue was recrystallized from ethanol/H_2O to give 12.9 g (40.5%) of 3,4'-dimethoxybenzophenone. mp. 52-54 °C, IR (KBr) $\nu C{=}O$ 1560 cm^{-1}. ^1H-NMR ($CDCl_3$, TMS, δ, ppm) 3.85 (3 protons, OCH_3 of the 3-methoxyphenyl group, s), 3.88 (3 protons, OCH_3 of the 4-methoxyphenyl group, s), 6.96 (2 aromatic protons, o to methoxy of the 4-methoxyphenyl group, d), 7.11 (1 aromatic proton, m to methoxy of the 3-methoxyphenyl group, m), 7.4 (3 aromatic protons, o and p to methoxy group of the 3-methoxyphenyl group, m), 7.84 (2 aromatic protons, m to methoxy group of the 4-methoxyphenyl group, d).

3,4'-Dimethoxydiphenylmethane

$AlCl_3$ (36.1 g, 0.271 mol) was slowly added to 100 ml of dry diethyl ether and the resulting solution was added dropwise from an additional funnel to a slurry of $LiAlH_4$ (4.8 g 0.126 mol) in 100 ml of dry diethyl ether under nitrogen atmosphere. To this reducing agent was added dropwise a solution containing 12.0 g (0.050 mol) of 3,4'-dimethoxybenzophenone in 50 ml of dry $CHCl_3$. The resulting suspension was stirred for 3 hr at room temperature. A mixture of 100 ml of concentrated HCl and 100 ml of H_2O was then carefully added to the reaction mixture. The ether layer was separated and the aqueous layer was washed with ether. The combined ether layers were washed three times with H_2O, dried over $MgSO_4$, filtered and the solvent was removed on a rotary evaporator. The resulting colorless oil represents 11.2 g (99.1%) of 3,4'-dimethoxydiphenylmethane which was used directly in the demethylation reaction ; ^1H-NMR ($CDCl_3$, TMS, δ, ppm) 3.76 (3 protons, OCH_3 of the 4-methoxyphenyl group, s), 3.77 (3 protons, OCH_3 of 3-methoxyphenyl group, s), 3.89 (2 protons, CH_2 , s), 6.7-6.9 (5 aromatic proton, o and p to methoxy group , m), 7.1-7.3 (3 aromatic protons, m to methoxy group, m).

3,4'-Dihydroxydiphenylmethane (BPM)

A solution of 3,4'-dimethoxydiphenylmethane (11.0 g, 0.048 mol) in 150 ml of dry methylene chloride was added dropwise under a dry nitrogen atmosphere to a dry ice - acetone bath cooled flask containing 96 ml (0.096 mol) of 1.0 M BBr_3 solution in methylene chloride . After the mixture was stirred over night at room temperature , enough H_2O was added to hydrolyze the excess BBr_3. A white solid precipitated out of solution. Diethyl ether was added to dissolve this solid, the organic layer was separated, and the aqueous layer was extracted with diethyl ether. The combined organic layers were washed three times with H_2O and dried over $MgSO_4$. Evaporation of the solvent in a rotary evaporator gave a pale brown powdery product. The crude product was recrystallized from water/ethanol using charcoal and recrystallized again from toluene using charcoal to give 5.8 g (61%) of white crystals of 3,4'-dihydroxydiphenylmethane ; mp. 116 °C; lit (13), 116°C, ^{1}H-NMR (acetone-d_6, TMS, δ, ppm), 3.73 (2 protons, CH_2, s), 6.5-6.9 (5 aromatic proton, o or p to hydroxy group , m), 7.0-7.2 (3 aromatic protons, m to hydroxy group, m).

1-(4-Hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl)ethane (MBPE)

MBPE of 100% purity (HPLC) was synthesized as described previously (2).

Synthesis of Polyethers and Copolyethers

Both polyethers and copolyethers were synthesized by liquid (o-dichlorobenzene) - liquid (aqueous NaOH) phase transfer catalyzed polyetherification. For the present experiments the polymerization time was 10-12 hr instead of 6 hr, the concentration of the tetrabutylammonium hydrogen sulfate was 15 mol% versus the phenol groups instead of 10 mol %, and the polymerization temperature was 80 °C. The other experimental details concerning the synthesis and purification of all polymers were identical to those described previously (2-6).

In the entire paper, copolyethers will be designated such as MBPE/3,4'-BPM(A/B)-8 where A/B refers to the molar ratio of the monomers MBPE to 3,4'-BPM. Therefore, polyethers will be either tabulated as MBPE/3,4'-BPM(100/0)-8 which represents the homopolymer of MBPE with 1,8-dibromooctane or simply mentioned as MBPE-8.

Techniques

200 MHz ^{1}H-NMR spectra were obtained with a Varian XL-200 spectrometer.

Molecular weights were determined by gel permeation chromatography (GPC). GPC analysis were carried out with a Perkin-Elmer Series 10LC equipped with a LC-100 column oven, LC 600 autosampler, and a Nelson Analytical 900 series data station. The measurement were made by using the UV detector, chloroform as solvent (1 ml/min, 40 °C), a set of PL gel columns of 10^2, 5 x 10^2, 10^3, 10^4 and 10^5 Å, and a calibration plot constructed with polystyrene standards.

A Perkin-Elmer DSC-4 differential scanning calorimeter equipped with a TADS data station Model 3600 was used to determine the thermal transitions. Heating and cooling rates were 20°C/min in all cases. First order transitions (crystalline-crystalline, crystalline-liquid crystalline, liquid crystalline-isotropic etc.,) were read at the maximum or minimum of the endothermic or exothermic peaks. Glass transition temperatures (Tg) were read at the middle of the change in heat capacity. First heating scans differ from second heating scans. This difference will be briefly discussed. A discussion of the influence of the thermal history of the sample on phase transitions was reported previously (3) for copolymers based on MBPE and two flexible spacers containing odd numbers of methylene units.

A Carl Zeiss optical polarizing microscope (magnification 100 x) equipped with a Mettler FP-82 hot stage and a Mettler 800 central processor was used to observe thermal transitions and to analyze the textures (23).

RESULTS AND DISCUSSION

Scheme I outlines the synthesis of all copolymers. Second heating and cooling DSC scans of the copolymers MBPE/3,4'-BPM(A/B)-8 are presented in Figure 1a, b. The characterization of both homopolymers and copolymers is summarized in Table I. The number average molecular weights of all polymers are above 20,000. These values are above the molecular weights which still influence the parameters of their phase transitions. The copolymer composition determined by 200 MHz ^{1}H-NMR spectroscopy agrees with that of the monomer feed since conversion were always higher than 95%. The interpretation of these DSC curves can be made best by following first the cooling scans (Figure 1b). MBPE/3,4'-BPM(100/0) to MBPE/3,4'-BPM(70/30)-8 display both isotropic-nematic and nematic-crystalline transitions. Copolymers MBPE/3,4'-BPM(70/30)-8 to MBPE/3,4'-BPM(30/70)-8 exhibit only an isotropic-nematic phase transition (Table I). On the heating scans copolymers MBPE/3,4'-BPM(100/0) to MBPE/3,4'-BPM(60/40)-8 exhibit a crystalline phase and a very narrow nematic mesophase. Copolymers MBPE/3,4'-BPM(50/50)-8 to MBPE/3,4'-BPM(30/70)-8 display only a nematic mesophase (Figure 1a). 3,4'-BPM-8 is only amorphous. The phase transition parameters of copolymers MBPE/3,4'-BPM(A/B)-8 are summarized in Table I and plotted in Figure 2a and b. The linear dependences of isotropic

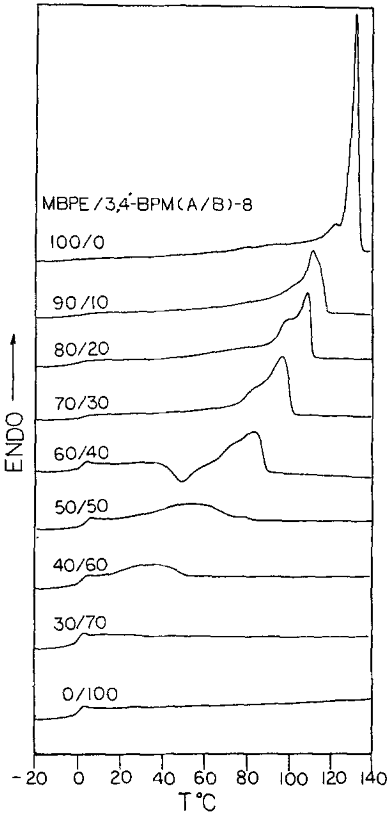


Figure 1a: Second heating DSC scans of MBPE/ 3,4'-BPM(A/B)-8

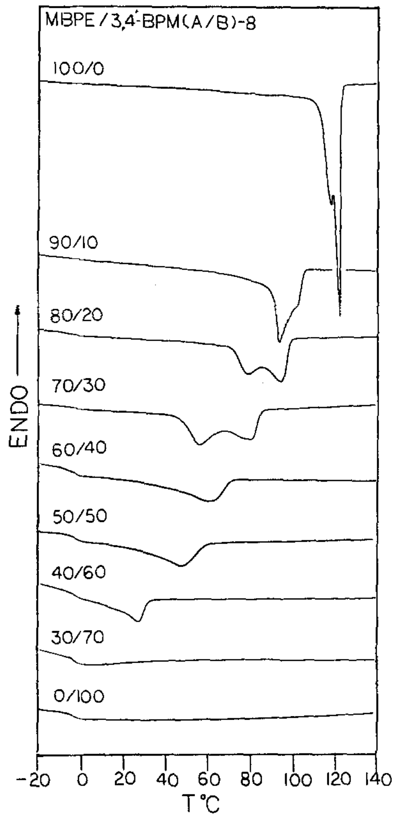


Figure 1b: Cooling DSC scans of MBPE/ 3,4'-BPM(A/B)-8

Table I Characterization of Polyethers based on MBPE and 1,8-Dibromooctane (MBPE-8), 3,4'-BPM and 1,8-Dibromooctane (3,4'-BPM-8) and of Corresponding Copolyethers [MBPE/3,4'-BPM(A/B)-8]

MBPE/3,4'-BPM(A/B)-8			Thermal transitions (°C), and corresponding enthalpy changes (Kcal/mru) in parentheses	
MBPE/3,4'-BPM	Mn	Mw/Mn		
Mol Ratio	GPC		Heating	Cooling
100/0	29,400	2.05	k 122 n 132(3.81^{a})i	i 119(3.53^{a}) n 116 k
90/10	21,500	2.34	g 0 k 104 n 110(3.33^{a})	i 101(3.24^{a}) n 95 k -3 g
80/20	33,800	1.72	g -1 k 99 n 107(2.96^{a}) i	i 94(2.74^{a}) n 78 k -7 g
70/30	23,900	1.85	g 1 k 82 n 96(2.95^{a}) i	i 80(2.77^{a}) n 57 k -3 g
60/40	30,800	1.77	g 1 k 58 n 71 (2.48^{a}) i	i 60(1.51) n -4 g
50/50	51,100	1.48	g 3 n 52(1.21) i	i 48(1.21) n -5 g
40/60	25,900	2.05	g 1 n 36(0.82) i	i 26(0.70) n -3 g
30/70	30,400	1.74	g 0 n 20(0.05) i	i 7(0.09) n -5 g
0/100	b)		g 1 i	i -2 g

a) overlapping transition ; b) insoluble in $CHCl_3$

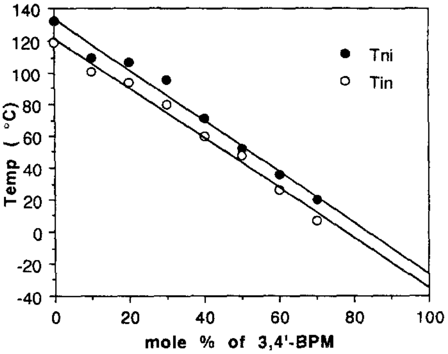


Figure 2a: Thermal transitions of MBPE/3,4'-BPM (A/B)-8

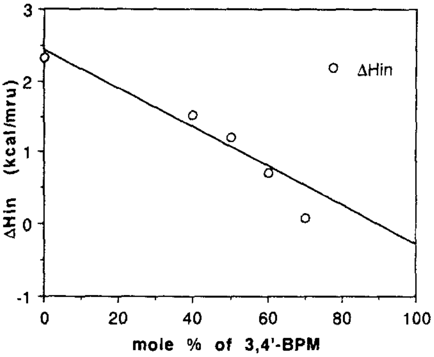


Figure 2b: ΔHin of MBPE/3,4'-BPM(A/B)-8

-nematic and nematic-isotropic transition temperatures on copolymer composition are presented in Figure 2a. Upon extrapolation to 3,4'-BPM-8, these plots may suggest the presence of a virtual mesophase which is located below the Tg of the homopolymer 3,4'-BPM-8. However, upon investigating the plot of ΔHin versus copolymer composition (Figure 2b), the virtual mesophase of 3,4'-BPM-8 would have an ΔHin=0. Therefore 3,4'-BPM-8 is indeed only amorphous and does not present a virtual mesophase. This experiment demonstrates that the parameters of the virtual mesophases of homopolymers determined by copolymerization experiments are accurate. It is however interesting to observe that the MBPE/3,4'-BPM(A/B)-8 copolymers display a nematic mesophase up to a very high concentration of 3,4'-BPM, although 3,4'-BPM-8 homopolymer is only amorphous. This result is due to the fact that the structural units of these copolymers are isomorphic within the nematic phase over a very large range of compositions. This result is in agreement with similar results from the field of crystalline binary copolymers which are derived from structural units which lead to a crystalline and respectively an amorphous parent homopolymer. However, since the structural units of these copolymers are isomorphic over a quite broad range of compositions they lead to a crystalline copolymer (24,25).

Figure 3 presents the second heating and cooling DSC traces of the copolymer MBPE /4,4'-BPA(A/B)-8 . The interpretation of their phase behavior was performed as for the previous system. The experimental results are summarized in Table II. The temperature transitions associated with the nematic mesophase displayed by these copolymers show a linear dependence of composition. These data are plotted in Figure 4. The range of copolymer composition which can accommodate a mesophase is narrower than in the previous system. The enthalpy changes associated with the transitions of the nematic mesophase are plotted in Figure 5 and upon extrapolation lead to ΔHin=0 for 4,4'-BPA-8. Therefore, as demonstrated both by direct DSC measurements and by the extrapolation of the parameters associated with the nematic mesophase of MBPE/4,4'-BPM(A/B)-8 copolymers, the homopolymer 4,4'-BPA-8 is only amorphous.

Table II Characterization of Polyethers based on MBPE and 1,8-Dibromooctane (MBPE-8), 4,4'-BPA and 1,8-Dibromooctane (4,4'-BPA-8) and of Corresponding Copolyethers [MBPE/4,4'-BPA(A/B)-8]

MBPE/3,4'-BPM(A/B)-8 MBPE/3,4'-BPM	Mn	Mw/Mn	Thermal transitions (°C), and corresponding enthalpy changes (Kcal/mru) in parentheses	
Mol Ratio	GPC		Heating	Cooling
100/0	29,400	2.05	k 122 n 132(3.81^{a}) i	i 119(3.53^{a}) n 116 k
90/10	24,400	1.93	g 7 k 107 n 120(3.47^{a}) i	i 100(2.98^{a}) n 95 k 1 g
80/20	20,500	1.98	g 6 k 91 n 103(2.12^{a}) i	i 84(2.02^{a}) n 78 k 5 g
70/30	24,500	1.99	g 11 k 89 n 91(1.18^{a}) i	i 62(1.49^{a}) n 49 k 5 g
60/40	31,000	2.25	g 8 k 16 n 79 (0.60) i	i 43(0.26) n 7 g
50/50	26,000	1.94	g 13 i	i 5 g
20/80	18,400	1.63	g 17 i	i 10 g
0/100	13,200	1.85	g 25 i	i 17 g

a) overlapping transition

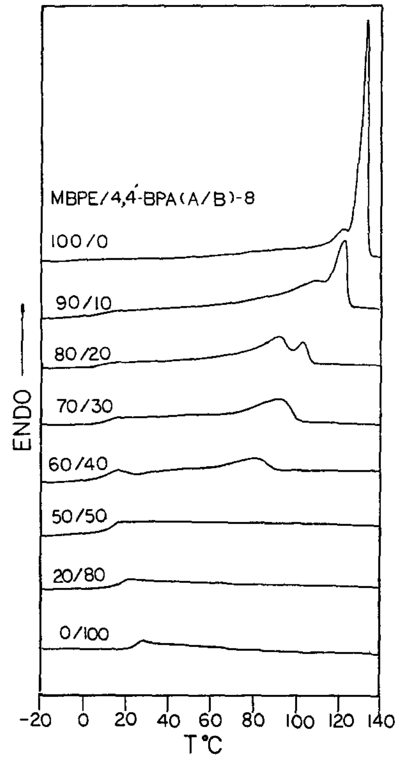


Figure 3a: Second heading DSC scans of MBPE/ 4,4'-BPA(A/B)-8

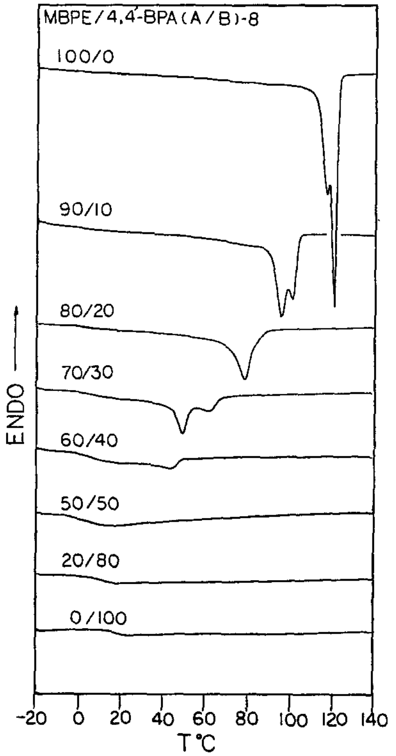


Figure 3b: Cooling DSC scans of MBPE/ 4,4'-BPA(A/B)-8

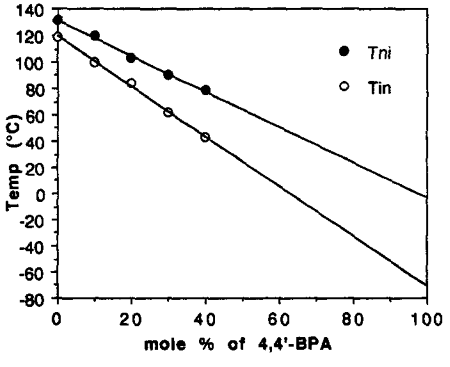


Figure 4: Thermal transitions of MBPE/4,4'-BPA (A/B)-8

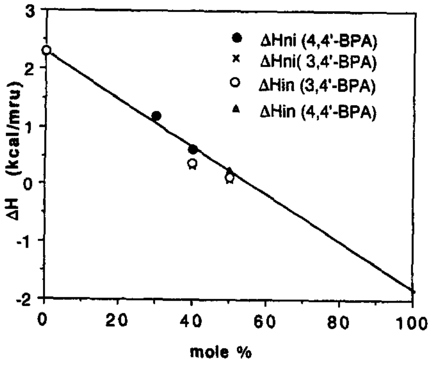


Figure 5: ΔHin and ΔHni of MBPE/4,4'-BPA (A/B)-8 and of MBPE/3,4'-BPA(A/B)-8

Finally, Table III summarizes the temperature transitions of the copolymers MBPE/3,4'-BPA(A/B)-8. Their second heating and cooling DSC scans are presented in Figure 6a, b. The thermal transitions associated with their nematic mesophases are plotted in Figure 7 while the corresponding enthalpy changes in Figure 5. These results demonstrate again that the structural units of this copolymer are isomorphic within the nematic phase over a broad range of compositions although the 3,4'-BPA-8 homopolymer is only amorphous.

Table III Characterization of Polyethers based on MBPE and 1,8-Dibromooctane (MBPE-8), 3,4'-BPA and 1,8-Dibromooctane (3,4'-BPA-8) and of Corresponding Copolyethers [MBPE/3,4'-BPA(A/B)-8]

MBPE/3,4'-BPA(A/B)-8 MBPE/3,4'-BPA Mol Ratio	Mn GPC	Mw/Mn	Thermal transitions (^{o}C), and corresponding enthalpy changes (Kcal/mru) in parentheses Heating	 Cooling
100/0	29,400	1.87	k 122 n 132(3.81^{a}) i	i 119(3.53^{a}) n 116 k
90/10	24,000	2.32	g 7 k 111 n 105(2.92^{a}) i	i 99(2.55^{a}) n 94 k 5 g
80/20	34,000	2.26	g 7 k 83 n 100(2.03^{a}) i	i 81(2.05^{a}) n 76 k 4 g
70/30	27,000	1.62	g 10 k 74 n 88(1.23^{a}) i	i 64(1.42^{a}) n 58 k 4 g
60/40	32,900	3.19	g 11 n 51(0.31) i	i 42(0.37) n 4 g
50/50	42,500	1.51	g 10 n 43(0.08) i	i 20(0.12) n 5 g
0/100	34,700	1.51	g 17 i	i 10 g

a) overlapping transition

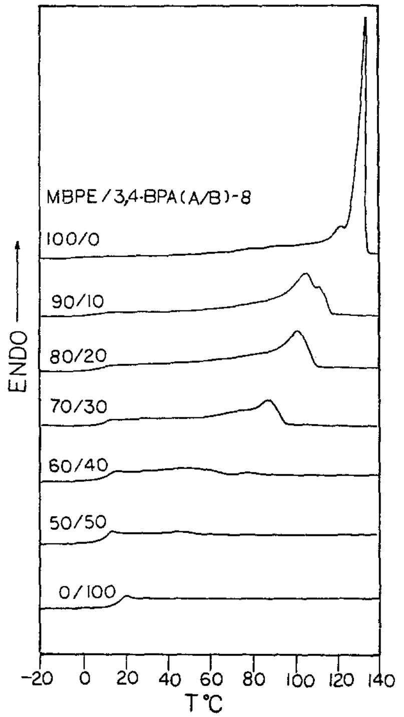


Figure 6a: Second heating DSC scans of MBPE/ 3,4'-BPA(A/B)-8

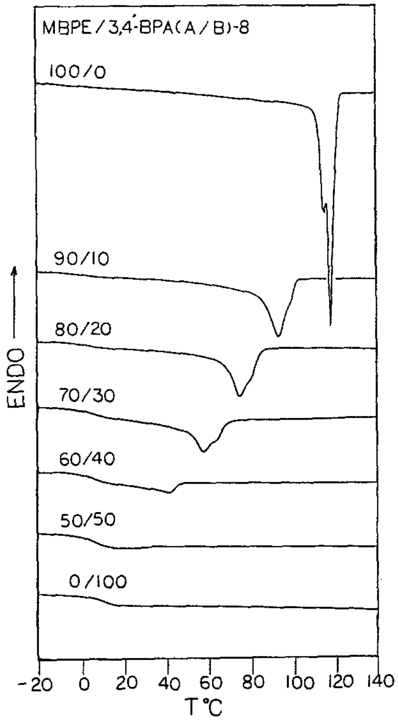


Figure 6b: Cooling DSC scans of MBPE/ 3,4'-BPA(A/B)-8

Finally some comments on the influence of the thermal history of the sample on the phase behavior of these copolymers. As observed from Tables I, II and III, the copolymers with molar ratios between the two bisphenols of about 50/50 display on the second DSC scans an enantiotropic nematic mesophase only. This is because their rate of crystallization is very low. After annealing of room temperature (i. e., above Tg) most of these copolymers crystallize. Several representative first heating scans obtained after 2 month of annealing at room temperature are presented in Figure 8. All copolymers present a crystalline melting followed by a nematic mesophase.

The general conclusion derived from these experiments is that nonmesogenic bisphenols can be incorporated into the structure of liquid crystalline copolymers, and phase behavior of these copolymers is governed by the same rules as those of other classes of liquid crystalline copolymers (2-11). That is, over the range of compositions where the structural units are isomorphic within the mesophase the resulting copolymers display a mesophase whose parameters are weight averaged over those of the parent

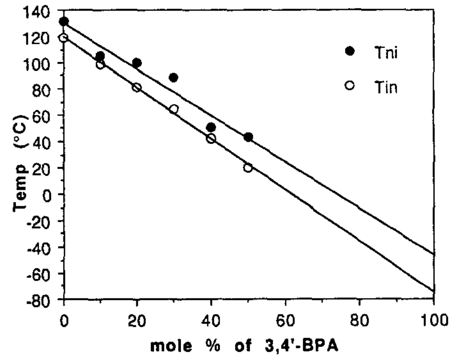


Figure 7: Thermal transitions of MBPE/3,4'-BPA (A/B)-8

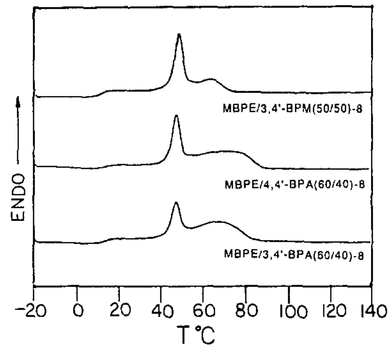


Figure 8: First heating scans after 2 month annealing at room temperature

homopolymers. MBPE/3,4'-BPM(A/B)-8 copolymers form a nematic mesophase over the broadest range of temperatures, followed by MBPE/3,4'-BPA(A/B)-8 and MBPE/4,4'-BPA(A/B)-8. This is most probably because the 3,4'-disubstituted bisphenols can adopt a more linear conformation for one of their conformers than the corresponding 4,4'-disubstituted bisphenols (Scheme I).

ACKNOWLEDGEMENTS

Financial support from the National Science Foundation, Polymer Program (DMR-86-19724), and Japan Synthetic Rubber Co., Ltd., is gratefully acknowledged.

REFERENCES

1) V. Percec and R. Yourd, Macromolecules, 21, 3379 (1988)
2) V. Percec and R. Yourd, Macromolecules, 22, 524 (1989)
3) V. Percec and R. Yourd, Macromolecules, 22, 3229 (1989)
4) V. Percec and R. Yourd, Makromol. Chem., in press
5) V. Percec and R. Yourd, Makromol. Chem., in press
6) V. Percec and Y. Tsuda, Macromolecules, 23, 5 (1990)
7) V. Percec and Y. Tsuda, Polym. Bull., 22, 489 (1989)
8) V. Percec and Y. Tsuda, Polym. Bull., 22, 497 (1989)
9) V. Percec and Y. Tsuda, Polym. Bull., in press
10) V. Percec and Y. Tsuda, Macromolecules , in press
11) V. Percec and Y. Tsuda, Polymer, submitted
12) C.K. Ober, J. I. Jin and R. W. Lenz, Adv. Polym. Sci., 59, 130 (1984)
13) W. J. Jackson, Jr., Mol. Cryst. Liq. Cryst., 169, 23 (1989)
14) M. Ballauff, Angew. Chem. Int. Ed. Engl., 28, 253 (1989)
15) C. Noel, Makromol. Chem., Macromol. Symp., 22, 95 (1988)
16) H. Finkelmann, Angew. Chem. Int. Ed. Engl., 26, 816 (1987)
17) H. Ringsdorf, B. Schlarb and J. Venzmer, Angew. Chem. Int. Ed. Eng., 27, 113 (1988)
18) R. W. Lenz and J. I. Jin, Macromolecules, 14, 1405 (1981)
19) T. D. Shaffer, M. Jamaludin and V. Percec, J. Polym. Sci: Part A: Polym. Chem., 23, 2913 (1985)
20) J. Watanabe, K. Ikeda and W. R. Krigbaum, J. Polym. Sci: Part B: Polym. Phys., 25, 19 (1987)
21) W. Zhang, J. I. Jin and R. W. Lenz, Makromol. Chem., 189, 2219 (1988)
22) J. I. Jin and J. H. Chang, Macromolecules, 22, 4402 (1989)
23) D. Demus, L. Richter, "Textures of Liquid Crystals", Verlag Chemie, Weinheim, 1978
24) G. Allegra and I. W. Bassi, Adv. Polym. Sci., 6, 549 (1969)
25) G. Allegra and I. W. Bassi, in "Polymer Handbook", J. Brandrup and E. H. Immergut Eds., Wiley, New York, 1975, p. III-205

Accepted April 12, 1990 C